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SOME OPTICAL AND MECHANICAL PROPERTIES OF POLYVINYL CHLORIDE

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January, 1965



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FOREWORD

The photoelastic properties of polyvinyl chloride (PVC) had been subjected to preliminary investigation by the principal investigator several years ago^{1,2,3,4}. On the basis of this, some of these measurements were repeated and extended by Mr. Utsuo during the past year while he was on leave from the Japan Leather Company to work in the laboratories of the Polymer Research Institute. These measurements confirm previous observations and demonstrate the contribution of both distortional and prientational contributions to the birefringence. They also indicate the possibility of dishroism studies on partly decomposed PVC which will be described in a future report. Measurements of dynamic birefringence were also conducted indicating a negative strain-optical coefficient at room temperature consistant with a dominent distortional contribution.

Richard S. Stein

SOME OPTICAL AND MECHANICAL PROPERTIES OF POLYVINYL CHLORIDE

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1. INTRODUCTION

Some observations of the optical and mechanical properties of polyvinyl chloride (FVI) were carried out, including the birefringence change with stretching at various temperatures, the thermal stress and birefringence cycle within the temperature range between room temperature and about 100°C., the dynamic stress and birefringence at room temperature and the preliminary experiment on visible and infrared dichroism change with stretching. Concerning the last two, unfortunately, positive results could not be obtained so far.

2. MATERIALS

The FVI used for these studies was a commercial product named "Opalon 660" high molecular weight FVI homopolymer of Monsanto Company. Some of the typical properties of this polymer are listed in Table I.

TABLE I

Some Typical Properties of "Opalon 660"

Specific gravity	1.40
Specific viscosity	0.55
Bulk density	0.47
Volatility % wt. loss on heating	0.15

*Solution of 0.40g of polymer in 100 ml of cyclohexanone at 25°C.

On leave from Japan Leather Institute, Tokyo 1963-64 (Present address)

*Supported in part by a contract with the Office of Naval Research and in part by grants from the Petroleum Research Fund, the Air Force Office of Scientific Research and the Army Research Office (Durham).

This FVC was purified by reprecipitation from tetrahydrofuran solution using methyl alcohol as a precipitant three times. The solvents used were purified by means of fractional distillation at least twice. This sample is the same one as was used for studies of spherulite growth from FVC solutions⁶.

Sample films were prepared from the tetrahydrofuran solution by pouring onto a glass plate floating on the surface of mercury. The thickness of the films were controlled between 1.5 and 7 mil. depending upon the purpose of the experiments. The infrared and ultraviolet absorption spectra were investigated to confirm that the films were free from solvents and conjugated double bonds.

3. STRESS-STRAIN, STRAIN-BIREFRINGENCE AT VARIOUS TEMPERATURES

The stress-strain relationships were determined by an "Instron" tensile testing machine. The birefringence change with stretching was investigated by a Babinet Jompensator attached to "Instron" tensile testing machine using monochromatic light (5-51 $^{\circ}$), which was polarized at an angle of 45 $^{\circ}$ to the direction of stretching and passed through the sample. The sample was held in a glass-windowed chamber through which air may be circulated so as to maintain constant temperature. The details of the procedure are described elsewhere. The temperatures investigated were room temperature (26-27 $^{\circ}$ J.), 40 $^{\circ}$, 60 $^{\circ}$, and 80 $^{\circ}$ J. respectively. The stress-strain relationships obtained at various temperatures are plotted in Figure 1. The elongation is expressed in terms of percentage of unstretched length. The stress is in units of Kg/cm $^{\circ}$ of actual (stretched) cross sectional area (actually determined).

In the cases of the experiments under 40°1, the rate of stretching was controlled at 1% per minute. If samples were stretched at a rate greater than this, almost all of them broke at about 3% elongation. The minimum rate of the crosshead of our "Instron" tensile tester was 0.02" per minute, therefore the experiment was carried out using the sample strip of 2" in length xlcm width. In both cases,

a necking-like phenomenon was observed at about 3% elongation. At room temperature the sample broke at about 7% elongation. At 40°3, however, the sample could be stretched without breaking, after necking occured up to 150% elongation. Above 60°C, the measurements were carried out at an elongation rate of 2% per minute for which the pross-head speed was 3.02" per minute and the length of sample films was 1". The samples could be stretched without breaking up to several hundred percent of elongation. The Young's moduli obtained are listed in Table II.

TABLE II
Young's Moduli of FV3 at Various Temperatures

Temperature	Young's Modulus dynes/cm ²
Room Temperature (25~2~°3.)	4.6 x 10 ⁹
_2°2,	3.7 x 10 ⁹
ố0°∶.	2.4 x 10 ⁸
Eco.	6.9 x 10 ⁷

The birefringence change with stretching up to 2% elongation and birefringence thange on relaxation process at room temperature are shown in Figure 2. The stress and birefringence change with stretching up to 150% elongation at 40°C. are also plotted in Figure 3. In the case of the observation at room temperature, it is seen that a negative birefringence is observed and its value is kept almost constant during the period of a relaxation. At 40°C, also a negative birefringence is observed initially up to about 4.5% elongation, but after that it becomes positive and intreases monotonically with elongation. This change in birefringence coincides well with the beginning of a necking-like phenomena in stress-strain curve.

In Figure 2, the stress, birefringence changes with stretching and relaxation at higher temperatures are plotted. In those cases, no initial negative birefringence is observed. The birefringence decreases during relaxation although the absolute values is very small. This tendency coincides with that of nylon-6.

The values of (birefringence/stress) at 60° and 80°C, are plotted against elongation in Figure 5. A maximum value is observed for each curve at about 80% elongation. This fact suggests that the mechanism of elongation below 80% elongation is different from that above 80% elongation.

As a conclusion, the initial negative value of birefringence at lower temperature may be due to a distortional birefringence, and this negative value is very interesting. In the cases at higher temperatures, the birefringence is always positive, which means that a PVI segment is more polarizable parallel to the chain direction than perpendicular to it.

This behavior is similar to that which has been observed previously for several other polymers such as polyethylacrylate4, polymethyl methacrylate9,10 and polystyrene 12,13,1-. The differing origin of distortional and orientation birefringence have been dispussed 15,16,17. The negative birefringence observed at low temperatures is a consequence of distortion of a glassy polymer and involves such mechanisms as bond bending and internal rotation and separating molecules by opposing the intermolecular van der Waals forces. The positive birefringence at higher temperature is a consequence of the fact that the increased molecular mobility at these temperatures permits orientation of larger molecular segments within the time scale of the emperiment and that these segments are positively birefringent (having their greatest polarizability in the direction of the polymer chain as might be expected from the structure of PIC). The increasing positive birefringence with increasing temperature of stretching may be a consequence of the greater degree of orientation produced but may also result from the melting of crystals of polyvinyl chloride contributing negatively to the birefringence. Some evidence for this latter explanation will be presented in the next section.

The maximum in the (Δ n/stress) curves of Figure 5 is consistant with the orientation of a polymer containing stiff anisotropic elements such as crystals or "proto-crystals" consisting of long rigid or associated sections of chain and is comparable for example with the manner in which the birefringence and stress change upon stretching crystalline polyolefins. For a rubber having gaussian behavior, the stress and birefringence increase at the same rate upon stretching 15. However, for a suspension of crystallites in a rubber-like medium, the initial birefringence increase will be more rapid than the stress giving rise to an increase in the (Δ n'stress) ratio. However, the rate of increase of birefringence will decrease as the crystals approach total orientation while the stress will continue to increase at an increasing rate, giving rise to a subsequent decrease in the (Δ n'stress) ratio. This latter behavior also is found for rubbers²⁴ at high extension or stiff chains where non-gaussian behavior is evident^{19,20,21}.

-. THE THERMAL STRESS AND BIREFRINGENCE DYCLE

The thermal stress and birefringence cycles for several different elongations were investigated within the temperature range from room temperature to 105°C..

The sample was allowed to stand for more than one hour at 80°C, before measurement was made, stretched to a given elongation, and relaxed for two hours at this temperature. After that, both the stress and birefringence were determined as a function of temperature. The experimental apparatus and condition were the same as in the case of the measurement of stress-strain and birefringence relationships except that aluminum plates which had a pin hole were used instead of glass plates as even windows. This was done because the birefringence of the glass windows resulting from thermal strain was found to contribute appreciably. The rate of temperature change was controlled to 1°C, per minute. A copper-constantan thermocouple was used to measure the temperature and it was set as near as possible to the position on the surface of sample where the light beam for birefringence measurement was passed.

The thermal stress cycles and birefringence cycles for 200, 400 and 600% elongations are shown in Figure 6 and 7 respectively. In Figure 6, the tendencies of the stress change with temperature agree with the previous study . However. the tendencies in thermal birefringence cycles obtained slightly differ from the results previously reported 22,23. An irreversible decrease in birefringence rather than an increase is observed when the temperature of relaxation is exceeded in the present experiment. It is seen that the slopes of the birefringence-temperature relationships differ above and below the glass transition temperature. The previously observed irreversible increase in the birefringence of unplasticized polyvinyl chloride has been interpreted as resulting from the production of distortional strain during the initial elongation which is then relieved irreversibly upon heating above the elongation temperature by molecular flow producing additional orientation accompanied by an irreversible birefringence increase. Similar observations have been made on substituted polyamides and on polyethyl acrylate at low temperatures 22,23. With plasticized PVC, however, the birefringence irreversibly decreases, rather than increasing upon heating. This is a consequence of the plastitizer permitting more easy molecular flow with less distortion in the initial elongation. The irreversible birefringence decrease observed in the present studies may result from the molecular weight of the present sample being somewhat lower permitting more relaxation prior to heating.

The present observation that the birefringence reversibly decreases upon cooling at constant length is consistant with previous observations 1,4,23. Presumably the degree of crystallinity of the polyvinyl chloride increases upon cooling. This should result in an increase of birefringence as observed for rubber 20,24 and for substituted polyamides 1,23 unless (a) the crystals grow with their chain axes oriented in the stretching direction but have negative birefringence (greatest refractive index perpendicular to the chain direction) or (b) the crystals are positively birefringent

but grow with their chain axes oriented perpendicularly to the chain direction. If (a) is true, this must mean that the birefringence of a FVC chain in a crystal must be of opposite sign from that in the amorphous polymer, since the total birefringence of FVC is obviously positive as seen from the present and previous data. This could occur as a consequence of the possible appreciable contribution of anisotropic internal field to crystal birefringence 25,26,27. The situation (b) has been observed in the case of the crystallization of crosslinked polyethylene at low extensions, where the prystals are found to grow with their chain axes perpendicular to the orientation direction 25. However, such crystallization should cause an increase in stress rather than the slight decrease seen in the higher temperature regions of Figure 6. (The increase observed at lower temperatures is undoubtedly a consequence of the thermal contraction of the sample having a modulus which increases with decreasing temperature as one passes through the glass temperature as has been previously observed 1,4). Furthermore, if perpendicular orientation of the organisms, the amount of this should decrease with increasing elongation whereas the positive slope of the birefringence-temperature curves in Figure 7 is seen to increase with elongation. X-ray diffraction studies with varying temperature would be desirable to establish whether alternatives (a) or (b) are reasonable.

Another possibility, (c), is that the birefringence of the statistical segment of amorphous PVI may change with temperature because of the temperature dependence of the populations of its rotational isomers. The existance of such rotational isomers and the dependency of their concentration upon temperature has been demonstrated. The effective size and anisotropy of the statistical segment is dependent upon the concentration distribution of rotational isomers. In this way it is conceivable that the birefringence of the amorphous PVC chains may decrease as the temperature is lowered (favoring the more extended and more anisotropic isomers).

It is suggested that birefringence measurements on crystals of model compounds similar to those used by Krimm for his infrared studies²⁹⁻³² would be useful for testing this hypothesis.

A fourth possibility, (d), is that the birefringence changes with temperature because of the increasing negative birefringence distortional contribution as the temperature is lowered. This accompanies the increasing stress on the sample (seen in Figure 6) as the temperature is lowered past the glass temperature which results from the tendency for thermal contraction of the sample accompanied by an increasing modulus as the temperature is lowered. It is not probable that this is the major contribution, however, since the stress does not begin to increase with decreasing temperature until about 60-70°C. (Figure 6). However, as seen in Figure 7, the birefringence decreases at all temperatures starting at 105°C. where there is not likely to be an appreciable distortional contribution, since this is above T_g. There appears to be a slight increase in the rate of decrease at about 80°C. indicating perhaps a small distortional contribution.

Calculated values of birefringence temperature/stress $[(\Delta n)T/\sigma]$ for various stretching are plotted in Figure 8 as a function of temperature. It can be seen that within the temperature range between about 95°C, and 75°C, the values of $[(\Delta n)T/\sigma]$ on cooling process are almost independent of temperature. These constant values of $[(\Delta n)T/\sigma]$ are listed in Table III.

TABLE III

The Values of $[(\Delta n)T/\sigma]$ for Various Elongation When the Sample was Relaxed at 80°C. and Treated at 105°C.

Elongation	Stress/ (Δn) T relaxed at 80°C.	dynes/cm ² treated at 105°C.
200%	2.8 x 10 ⁷	1.7 × 10 ⁷
400%	5.2 x 10 ⁷	3.0×10^{7}
600%	7.6 x 10 ⁷	4.1 x 10 ⁷

As a reference, previously reported this value for polyvinyl chloride and some other polymers are shown in Table IV.

TABLE IV

The Values of Stress/ (Δn) T for Several Polymers

	$Stress/(\Delta n)T$	dynes/cm ²
Rubber	1.5 x	10 ⁷
Polyminyl chloride	3.0 x	107
Polyisobutylene	2.3 x	107
Polystyrene	-0.5 x	107

It can be seen that the values obtained are quite reasonable comparing Table III and IV. It is very interesting, however, that the value of $\sigma/\Delta nT$ are dependent upon the degree of elongation and temperature in the case of PVC, namely, it increases with increasing elongation and decreases with increasing treating temperature.

5. THE DYNAMIC STRESS AND BIREFRINGENCE AT ROOM TEMPERATURE

The dynamic stress and birefringence on PVC were investigated at room temperature within the frequency range between 0.00253 and 8.6 cycles per second. Techniques of the type previously described were used 34,35,36.

The purpose of these measurements was to determine the time dependence of the stress and birefringence change during the periodic deformation of the PVC samples. It appeared probable that the relaxation times for the distortional and orientational contributions would be different, and that dynamic measurements would serve to resolve these.

The thickness of sample film used was about 6 mil. One of the results obtained is shown in Figure 9. The measurement was carried out at a elongation of 2.04% for

length. The magnitude of vibration amplitude was 0.8% of elongated length. The general tendencies in dynamic mechanical properties are reasonable. It is noted that the value of the real part of the dynamic strain-optical coefficient, K', is negative and becomes more so with increasing frequency. This fact coincides with the fact that a negative birefringence is observed when PVC is stretched statically at room temperature up to 3% elongation. The negative K' is a consequence of the short relaxation time distortional contribution. At higher frequencies, there is less time for this contribution to relax out during the vibrational period, so the negative contribution is greater at high frequency. It is expected that at low enough frequency, K' would cross to positive values when the orientation contribution would dominate. The curves should be shifted to the right at higher temperatures (toward higher frequencies) and the positive K' values would then contribute at higher frequencies. Such temperature dependence peasurements would be of interest.

A maximum of the tan α curve (where α is the phase angle between birefringence and strain) is seen at about .01 cycles per second. There is some indication that the tan α curve is increasing toward a second maximum at higher frequencies.

The real part of the modulus, E', increases monatonically with increasing frequency and tan 5 (the phase angle between stress and strain) decreases indicative of a loss maximum at frequencies less than 0.001 cycles per second. It is likely that this low frequency loss maximum is associated with a chain orientation mechanism and it is probable that this is associated with the high temperature loss maximum ($\sim 85^{\circ}$ C. at about 0.2 - 15 cps) found by Schmieder and Wolf^{37,38} and Kono³⁹ associated with the glass temperature. It is expected that their smaller loss maximum at low temperature ($\sim -35^{\circ}$ C.) may correspond to the distortional process. It should be noted that this high temperature loss maximum is also probably associated with the infection in the stress relaxation curve found by Shen and Tobolsky ⁴⁰.

A very high temperature inflection is also seen by these latter workers and associated with a crystal melting point at 174° C. (which might be compared with a microscopically measured melting point of $191^{\circ} - 204^{\circ}$ C.).

6. DICHROISM OF VISIBLE LIGHT

In order to get some information about the molecular chain orientation with stretching, the measurement on the dichroism of visible light used \$1,42,43\$. In the case of FV3, however, two methods of sample preparation are available for this purpose. The first one is the method using FV3 sample thermally decomposed, second is the one using FV3 sample suitably dyed as same as in the cases of polyethylene terephthalate and other polymers. Concerning the first one, as well known, the thermal decomposition reaction of FV3 is assumed as a introducing reaction of conjugated double bonds into the polymer main chain by successive removing of hydrogen chloride \$40,440. These conjugated double bonds thermally introduced may be expected to locate in amorphous region of the matrix rather than the crystallites and also they might be expected as a source of a dichroism change of visible light with stretching. Therefore, a thermally treated FV3 sample film may be used for the measurement of the present purpose. Concerning the second method, however, there is no useful information about suitable dyes for this purpose at present. Therefore, thermally decomposed FV3 film was used for the present investigation.

The sample studied was a FVC film which was treated in a silicone oil bath for 30 minutes at 1-0 \pm 1°C.. The experimental procedures for the determination of dichroism were described elsewhere $^{11},^{12},^{13},^{15}$. The strain rate was 1% per minute and the temperature was 90°C..

The variations in the perpendicular and parallel intensities of light which passed through the sample were investigated over the period of time including the stretching process up to 200% elongation, relaxation for 90 minutes at 90°C. and

the thermal cycle process for 90°C. to 110°C. to 50°C. (the rate of temperature change was controlled within 1°C. per minute), and are plotted in Figure 11.

As a result, it becomes clear that this procedure is not suitable for the present purpose, although some appreciable changes in perpendicular and parallel intensities to the direction of elongation are observed. Some of the major reasons are as follows:

- (a) The mechanical properties of the thermally decomposed PVC differed from that of the original PVC. Some of them are listed in Table V. One of the thermal stress cycles at 200% elongation is shown in Figure 10 as a reference. The experimental procedure was the same as that mentioned above except that film was conditioned at 90° C. and stretched at this temperature. A thermal stress cycle for original PVC is compared with that of decomposed PVC using a broken line in the figure.
- (b) Some more decomposition reaction proceeded during the period of measuring including stretching, relaxation, and thermal cycle at such a high temperature as above 90°3...

TABLE V

Some Mechanical Properties of Original and Thermally Decomposed

Polyvinyl Chloride Film

	Original Film	Thermally Decomposed Film
Young's modulus	2.0 x 10 ⁷ dynes/cm ²	4.5 x 10 ⁸ dynes/cm ²
Tensile elongation	>600%	<400%
Tensile strength	Ca 300 Kg/cm ²	Ca 150 Kg/cm ²
Glass transition temperature*	Ca 75°C.	Ca 85°C.

^{*}This glass transition temperature was determined as a temperature at which a inflection on the thermal stress cycle is observed in Figure 10.

Since the solor of the sample lesame leepen during the experiment, it was impossible to calculate a accurate dichroism ratio. As a reference, one of the results obtained are plotted in Figure 11. [Recent measurements, by Mr. Ryo Yamada, which will be described in a later report, have been successful in obtaining values of dichroism for dehydrohalogenated PVC and PVC-ethylene copolymers.]

7. THE DICHROISM OF INFRARED AT ELEVATED TEMPERATURE

In order to get information of orientation of both crystalline part and amorphous part with stretching separately, the preliminary observation on dichroism changes of infrared 16,47 was performed on sample films which have been used for the measurements of birefringence changes. Because some of the infrared absorption bands between the wave length of 14 and 174 have been assigned as shown in Table VI 48-57. The measurements of their change with stretching might be useful for the present purpose.

TABLE VI Infrared Spectrum and Assignments for PVC Between the Wave Length 14 and 17μ

Wave Number	Wave Length	Polarization	Phase	Assignment
50: ===1	16.554	g a .	C	$\nu(CC1)B_1$
615	16.25	σ	A	v(CC1)S _{HH} (A)
638	15.68	σ	A	v(CCl)StH(A)
5-0	15.62	σ	C	v(CC1)A ₁
685	14.60	σ	A	v(CCl)S _{HC} (A)
693	14.43	×		

z : perpendicular A : amorphous

ca : band shows x dichroism at low draw ratio C : crystalline

x : parallel

v : stretching

A Ferkin Elmer 21 double beam spectrophotometer equipped with CsBr prism was used. A silver chloride polarizer was placed in the spectrometer between the light source and detector chambers. However, the shortest wave length which could be resolved by this CsBr prism system was 15μ . It was found that for the thickness of the films used, which was about $\frac{1}{2}$ mil., was too thick to get accurate absorption intensities of each bands within the wave length range between 15 and 17μ . The optimum thickness of the sample for this purpose should be 1 mil.

A plan for the major experiment was designed considering the following three points.

- 1) The thickness of the sample film should be about 1 mil.
- 2) The dichroism change with stretching at elevated temperature should be observed. These results obtained should be compared with the results of birefringence measurements.
- 3) In order to cover the wave length from 14 to 17 μ , a KBr prism should be used and the window of the oven should be KBr plates.

According to this plan a new sample extension mechanism in a small oven which can be set into the clearance between a AgCl polarizer and detector chamber of a Perkin-Elmer 21 double beam spectrophotometer, was constructed. Unfortunately, the equipment was not completed in time for the writer to complete his studies before leaving.

8. SUMMARY

1) A negative birefringence was observed initially when FVC was stretched at a temperature lower than 40°C. At higher temperature it showed positive birefringence, and the birefringence increased monotonically with stretching. As a result of the dynamic measurements at room temperature a negative value of K' also was observed and this value decreased with increasing frequency.

- 2) Thermal stress and birefringence cycles within the temperature range from room temperature to 105°C, were investigated. The general tendencies on thermal stress cycle coincided well with the results previously reported. Concerning thermal birefringence cycle, however, an irreversible decrease in birefringence rather than an increase was observed when the temperature of relaxation was exceeded. The constant values of ΔnT/σ were obtained within the temperature range between 75 and 95°C, on the cooling process. These values obtained are nearly equal to the value previously reported, but they seemed to be dependent upon the degree of elongation and treating temperature.
- 3) Dichroism change of visible light with stretching, relaxation, and thermal cycle was examined on the thermally decomposed PVC within the temperature range between 50 and 110°C.. As a result it became clear that the thermally decomposed FVC was not suitable and some suitably dyed PVC should be used for the present purpose.
- Although the measurements on the dichroism change of infrared with stretching at elevated temperature had been planned, unfortunately they could not be carried out.

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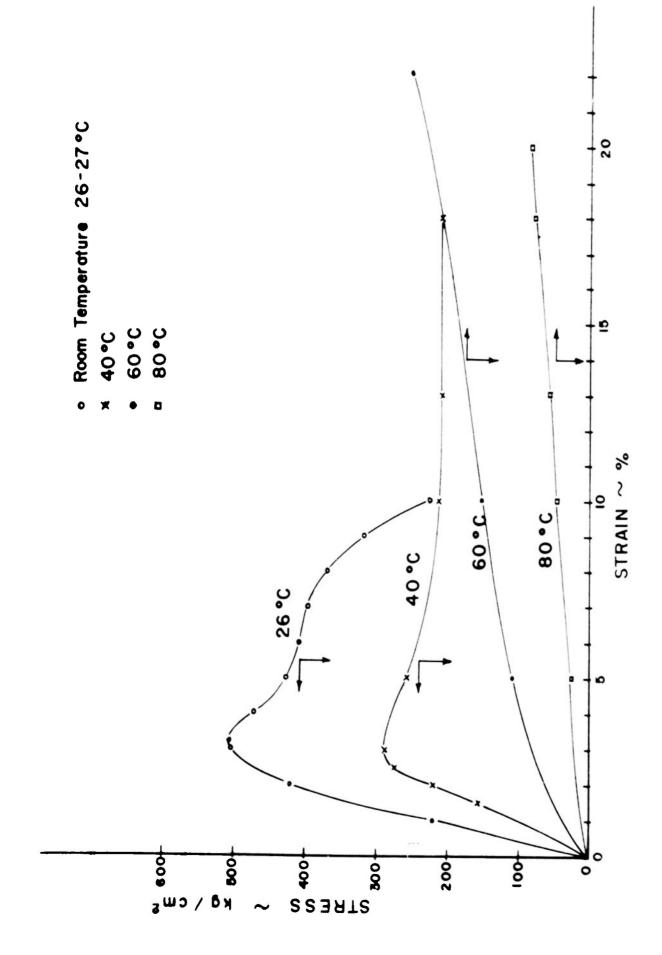
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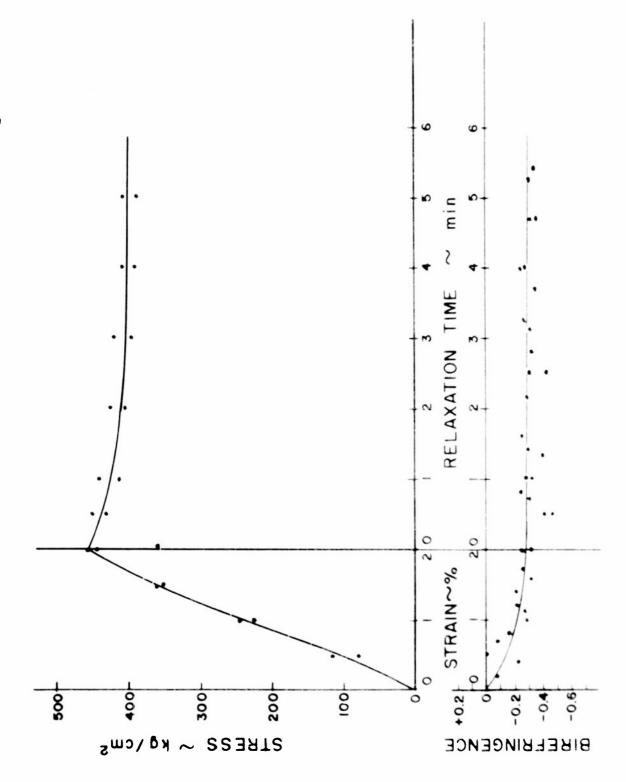
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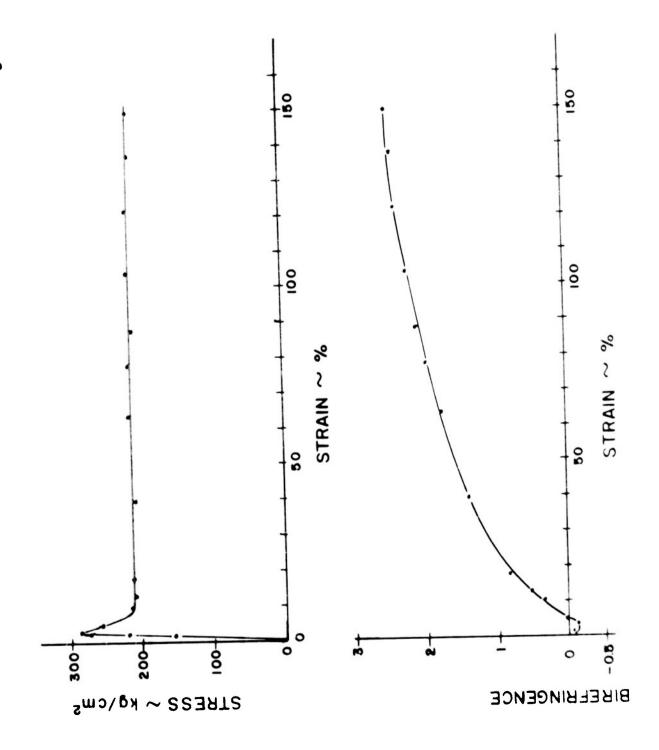
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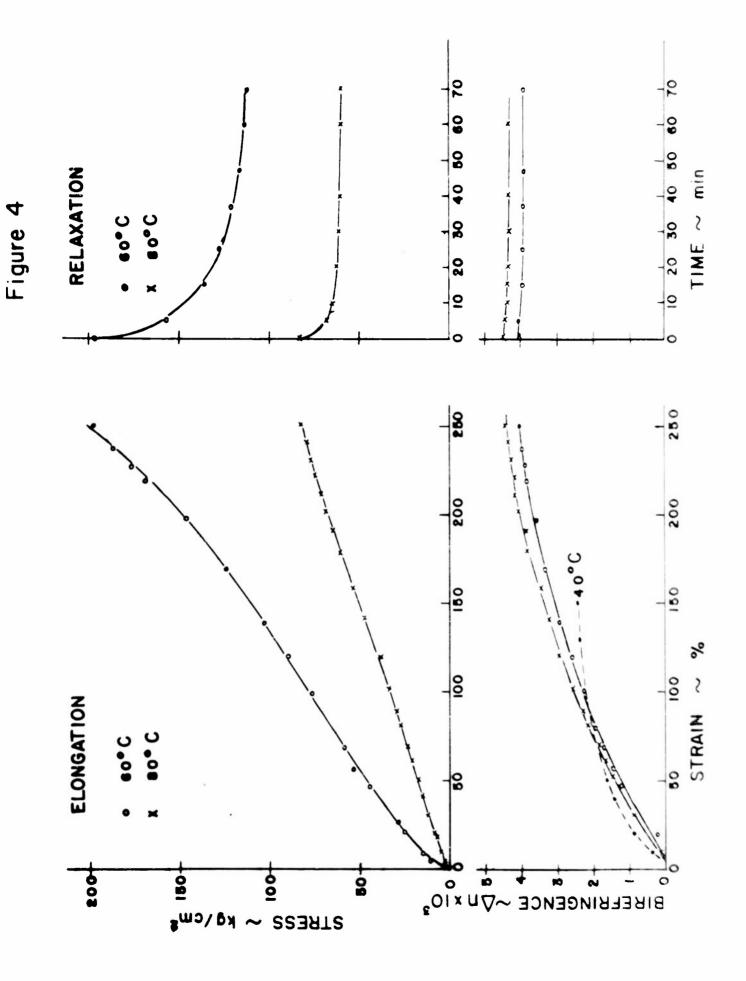
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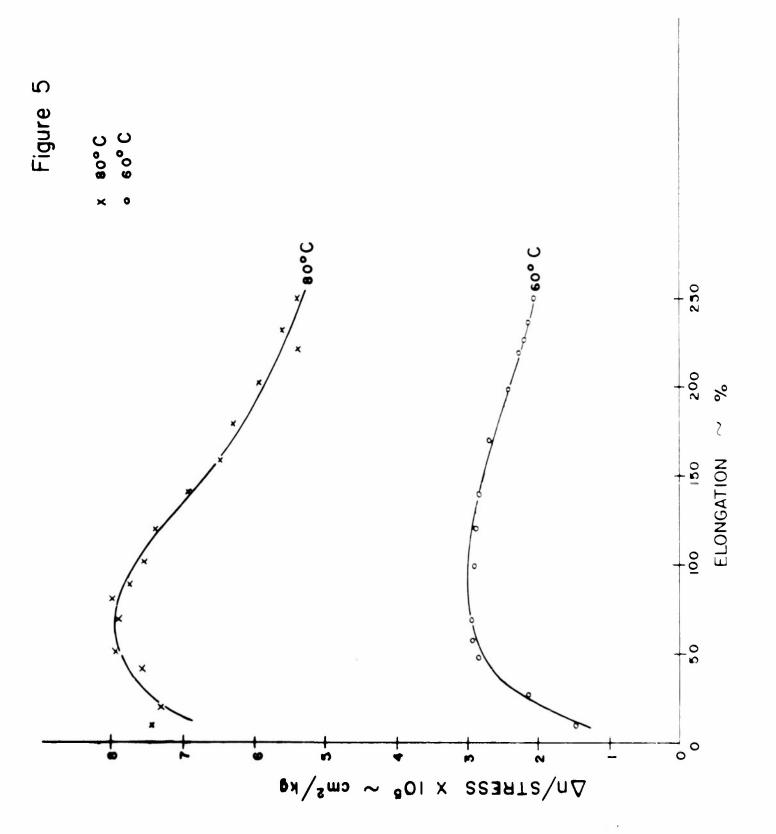
- Figure 1 The stress strain relationships up to about 20% elongation at various temperatures.
- Figure 2 The stress and birefringence change with stretching and relaxation at room temperature.
- Figure 3 The stress and birefringence change with stretching at 40°C.
- Figure 4 The stress and birefringence change with stretching and relaxation at 60 and 80°C.
- Figure 5 The variation of the value of birefringence/stress with stretching at 60 and 80°C.
- Figure 6 The thermal stress cycles for various elongations.
- Figure 7 The thermal birefringence cycles for various elongations.
- Figure 8 The variation of the values of birefringence x temperature per stress with temperature for various elongations.
- Figure 9 The variation of the dynamic stress and birefringence with frequency at room temperature.
- Figure 10 The thermal stress cycles of thermally decomposed and original FVC for 200% elongation.
- Figure 11 The variation of the perpendicular and parallel intensity of light which passed through the thermally decomposed PVC film with stretching, relaxation, and thermal cycle.

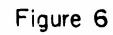


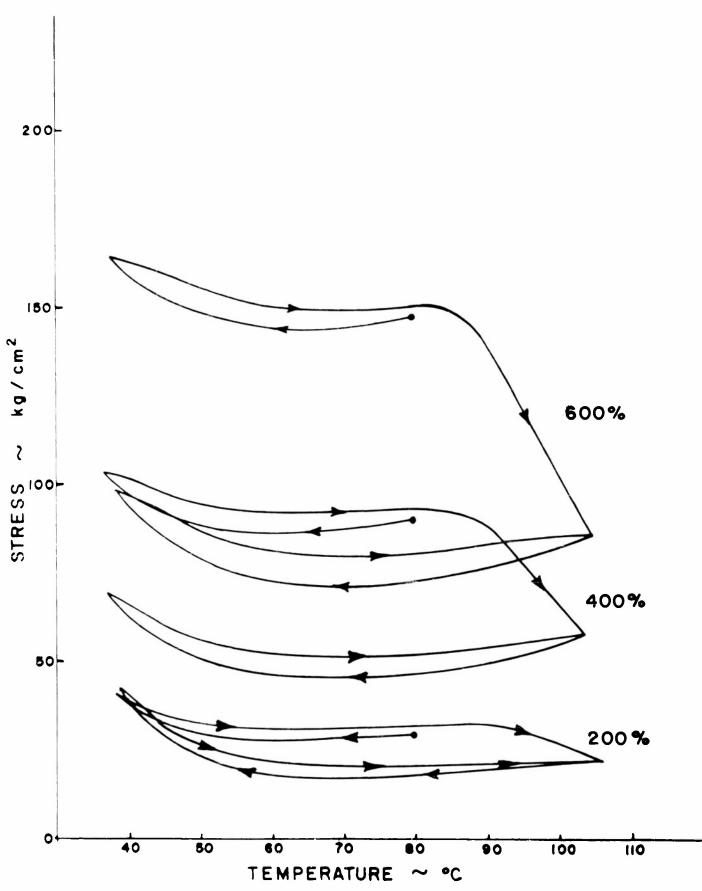


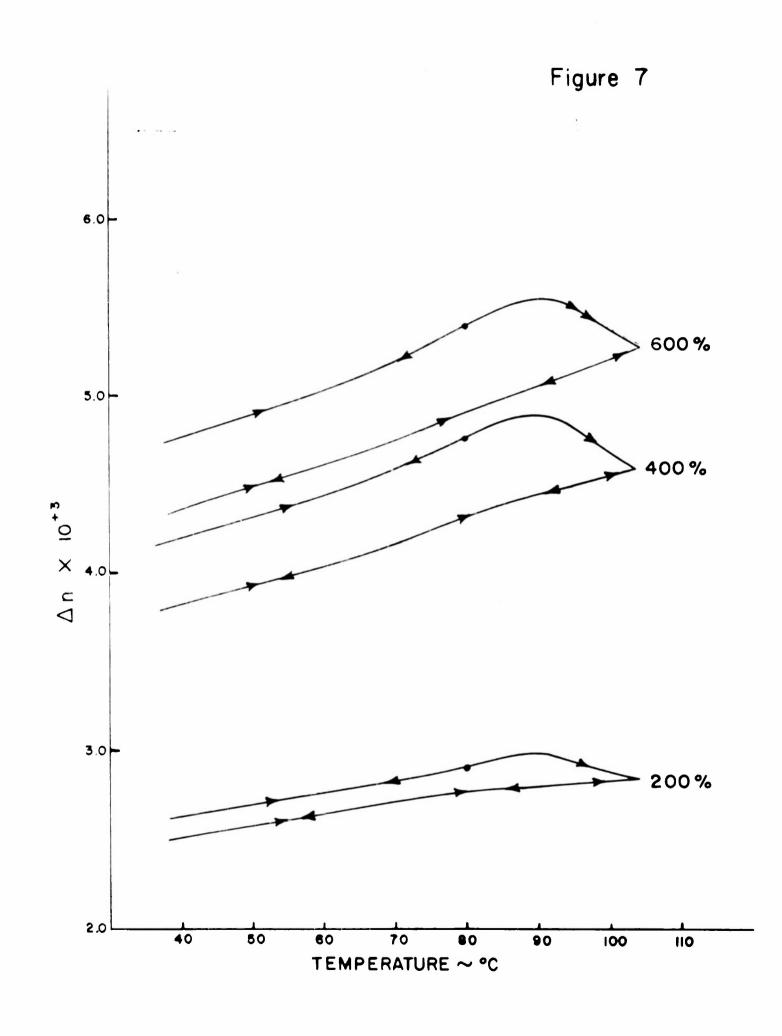


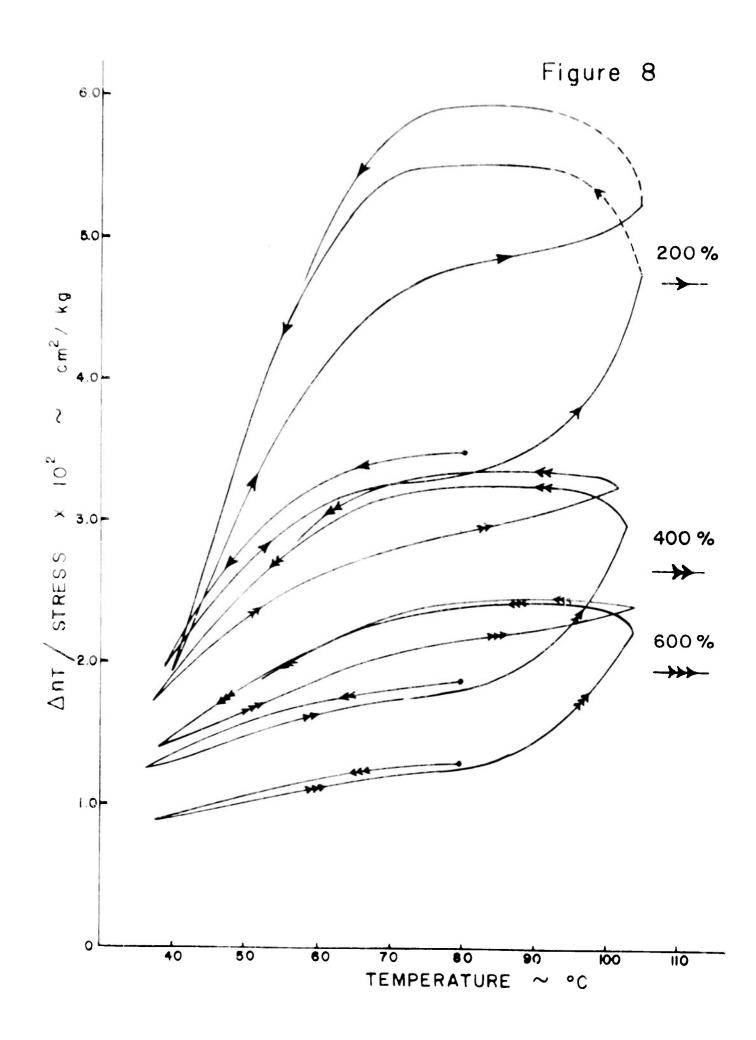












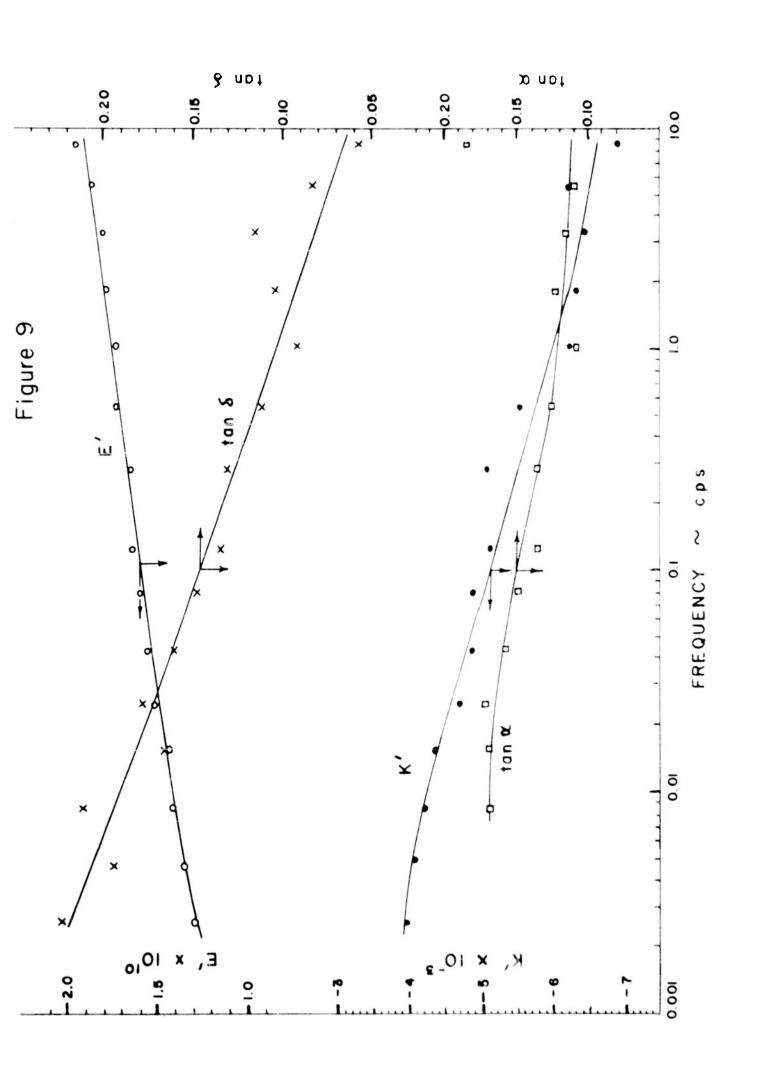
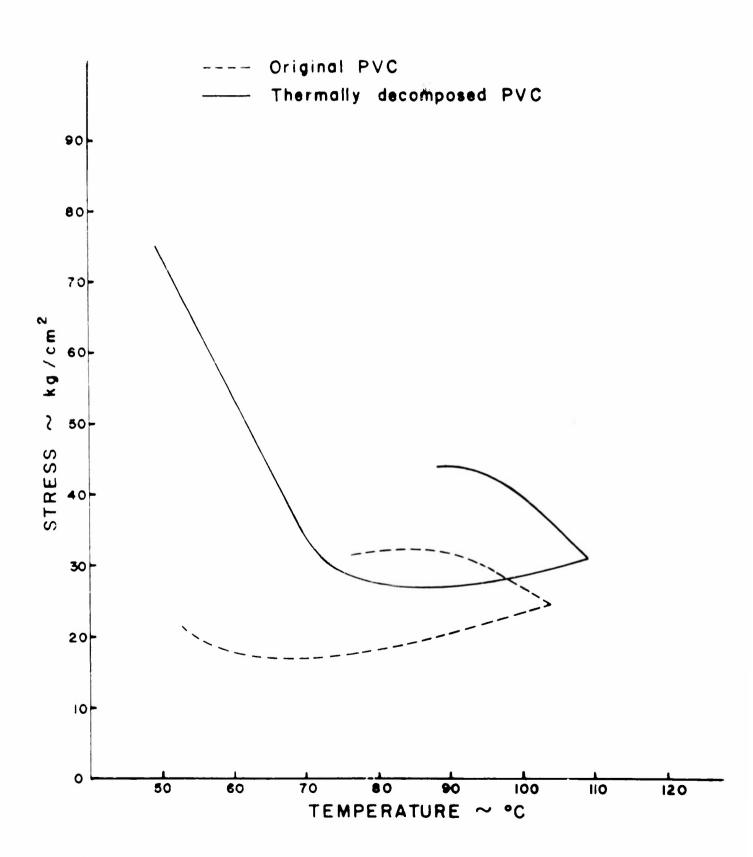
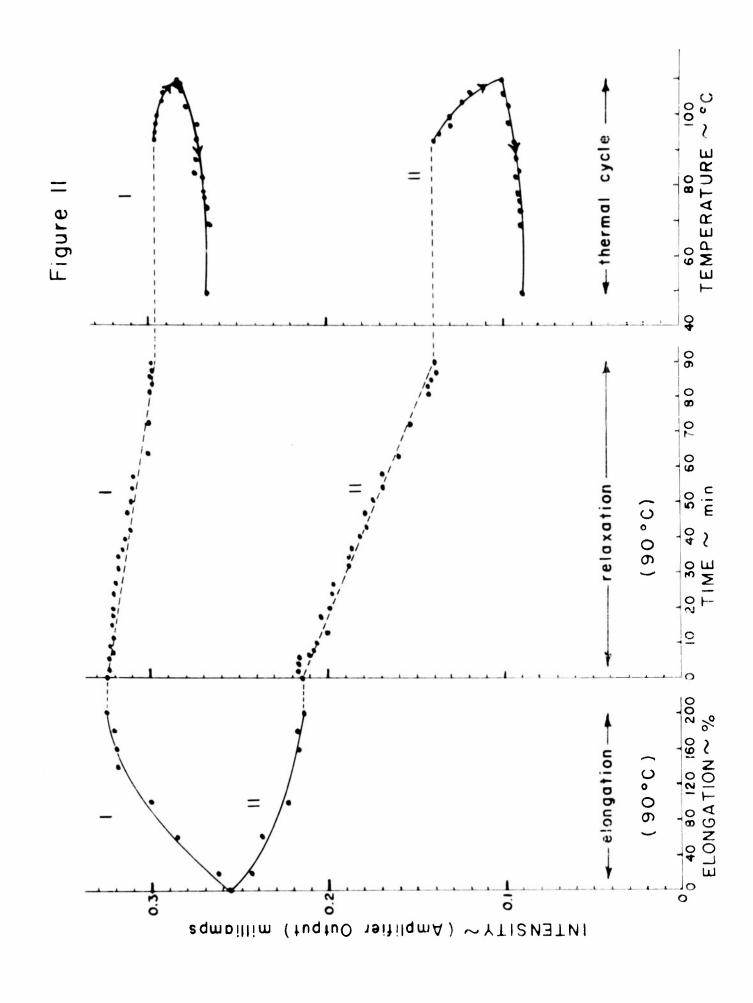


Figure 10





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